OPTIMIZATION OF THE MINERAL ACTIVATION PROCESS TO SEQUESTER CO$_2$ AT LOW PRESSURES AND TEMPERATURES
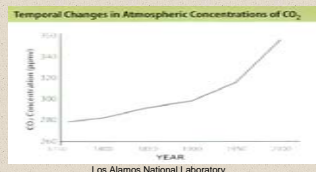
M. Mercedes Maroto-Valer[1], Matthew E. Kuchta[1], Yinzhi Zhang[1], John M. Andrésen[1], and Daniel J. Fauth[2]

PENNSTATE

[1]The Department of Energy and Geo-Environmental Engineering and The Energy Institute The Pennsylvania State University, University Park, PA 16802
[2]U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA 15236

Introduction

Temporal Changes in Atmospheric Concentrations of CO$_2$
Los Alamos National Laboratory

A 30% increase in atmospheric CO$_2$ concentrations has occurred since the Industrial Revolution, and concentrations continue to rise. Mineral carbonation is a promising CO$_2$ sequestration technology that involves the reaction of CO$_2$ with non-carbonate minerals to form stable mineral carbonates. Serpentine has been identified as a suitable feedstock, and the reaction is shown below.

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$
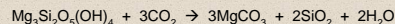
Advantages of the carbonation of serpentine minerals include the vast, readily available abundance of raw materials, the permanent storage of CO$_2$ as a stable mineral carbonate, and the overall process being exothermic, and therefore potentially economically viable.

Energy States of Carbon
National Energy Technology Lab / Department of Energy
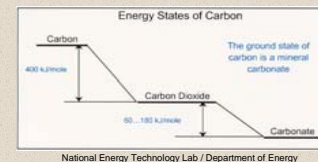
Mineral Sequestration Obstacles

⚜Kinetics - Innovative development of fast reaction routes under milder regimes in a continuous integrated process must be made.

⚜Carbonation Efficiency - Current carbonation studies require prior capture of the CO$_2$, high pressures, and extensive mineral particle communition, all energy-intensive operations.

The Active Carbonation Concept

⚜Promote and accelerate REACTION RATES and EFFICIENCIES through surface activation to the extent that extensive mineral particle communition is not required prior to sequestration.

⚜Surface activation by catalytic and physical means to accelerate the carbonation reaction efficiency.

⚜Physical activations were performed using steam, while chemical activations utilized various acids at room temperature.

BET Surface Area and Porosity Studies

⚜N$_2$ at 77K adsorption isotherms were obtained using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT.

Sample	BET Surface Area (m^2/g)	Pore Volume (mL/g)	Average Pore Diameter (nm)
Parent	8.2	0.017	8.5
Steam	15.8	0.035	8.8
Acid 1	329.5	0.234	2.8
Acid 2	79.5	0.085	4.3
Acid 3	121.7	0.097	3.2

⚜The surface area of the activated sample increased at least one order of magnitude for all the activated serpentines.

⚜The chemical activation appears to be more effective than physical activation in terms of increasing surface area and pore volume, while reducing the average pore diameter.

TGA Studies

⚜N$_2$ TGA profiles were obtained using a Perkin Elmer TGA 7 at a temperature range of 25°C to 900°C at 10°C/minute.

N$_2$ TGA Profiles - Activated Cedar Hills Serpentine
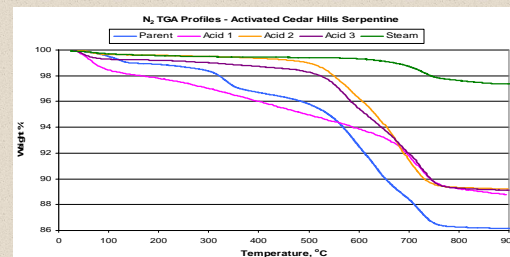
⚜The weight loss in the parent sample (~15%wt) is attributed to the removal of hydroxyl groups that inhibit the carbonation reaction by occupying active sites on the mineral surface.

⚜The chemically activated samples show a weight loss of around 11%wt and the loss is shifted to higher temperatures, indicating that the activation process selectively removed low-temperature (<600°C) hydroxyl groups.

⚜The physically activated sample shows a weight loss of around 3%wt, indicating that most of the water has been removed during activation.

Carbonation Studies

⚜High temperature and pressure analyses were carried out in a 1 L Hastelloy C-2000 continuous-stirred-tank-reactor (CSTR) unit, while low temperature and pressure carbonation reactions were performed in a 500 mL Hastelloy C-276 CSTR vessel.

Sample	Conversion Percentage	Carbonation Reaction Conditions (Temperature, Pressure)
Untreated	7.2	155°C, 126 atm
Steam (650°C)	59.4	155°C, 126 atm
Chemically Treated	52.5	20°C, 45 atm

⚜The samples underwent varying degrees of carbonation.

⚜The untreated parent sample underwent a 7% conversion at 155°C and 126 atm. Under identical conditions, the steam activated serpentine underwent a 60% conversion, illustrating the benefit of removing moisture from the serpentine. However, high temperature treatment is very energy intensive.

⚜CO$_2$ was also sequestered during the carbonation of the acid treated serpentine at much lower temperatures and pressures (20°C and 45atm).

SEM and XRD Studies

⚜SEM studies were conducted using a HiTACHI S-3500N, with an accelerating voltage of 20kV and a magnification of 1500X.

⚜XRD analyses were carried out on a Scintag Pad V unit with a vertical theta/2-theta goniometer.

Serpentine samples prior to carbonation   Serpentine samples after carbonation
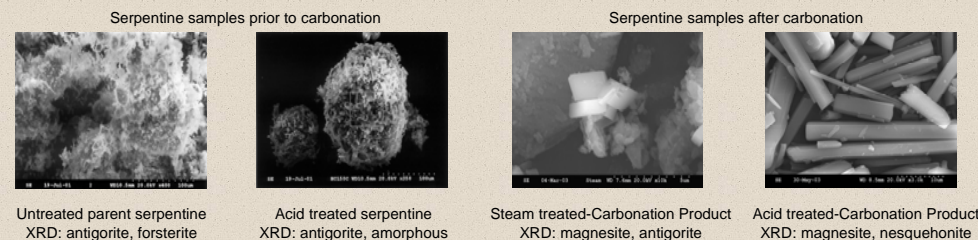
Untreated parent serpentine XRD: antigorite, forsterite | Acid treated serpentine XRD: antigorite, amorphous | Steam treated-Carbonation Product XRD: magnesite, antigorite | Acid treated-Carbonation Product XRD: magnesite, nesquehonite

⚜Images show that the structure of the activated serpentines has been significantly altered by the treatment process.

⚜The product from the carbonation of the steam activated serpentine (SCP-4) shows MgCO$_3$ cube-shaped crystals.

⚜The carbonation product from the acid treated serpentine shows MgCO$_3$ crystals with a much longer, rod-like appearance.

Conclusions

⚜The obstacles inhibiting mineral carbonation may possibly be overcome by activating the raw minerals to accelerate the carbonation reaction efficiency.

⚜Chemical activation appears to be the preferred method to increase surface area (330m^2/g, compared to only 8m^2/g for the raw serpentine), while physical activation results in a greater weight loss.

⚜The most promising results came from the carbonation of the H$_2$SO$_4$ treated serpentine , where a carbonation efficiency of nearly 53% was observed, comparable to the physically activated serpentine that showed a 60% conversion at 155°C under 126 atm of CO$_2$ pressure.

⚜A provisional patent (Serial No: 60467,809) has been filed and a full patent is currently being filed.

Future Work

⚜Optimization of the activate carbonation conditions.

⚜Development of a continuous CO$_2$ sequestration module.

⚜Conduct a preliminary economic assessment of the active carbonation process.

Acknowledgements